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Syngas production through steam and CO₂ reforming of methane over Ni-based catalyst-A Review

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Abstract. CH₄ and CO₂ are the two foremost greenhouse gases which are accountable for global warming. Controlling of their emissions and proper utilization has become significant challenge in the field of energy researches. Reforming of CH₄ with steam and CO₂ is one of the feasible solutions to convert the primary sources of greenhouse gases into syngas. Nowadays, syngas is an essential resource for many industrial applications to produce beneficial value-added products. Besides, it has been referred to as a transition from the fossil fuel towards pure hydrogen energy in the stationary internal combustion engines. Methane reforming with steam or CO₂ occurs as a result of the reaction between methane and steam or CO₂ in the presence of a catalyst at high temperature. Reaction routes need to be controlled to achieve the desired outputs. To control the reaction path, there are several parameters need to be technically optimized. Reaction kinetic is also necessary to find the reaction rate and select the convenience type of catalyst that can enhance the reaction rate. Catalyst selection and preparation are essential in the reaction because they contribute to the reaction outputs mainly of the syngas ratio (H₂/CO). This manuscript is intended to observe the trend of technology improvements on thermodynamic analysis and kinetic study of steam and CO₂ reforming of methane reactions over the Ni-based catalyst. It also presents the evaluation of the catalytic effect/properties and their relationship with the performance of the catalyst needed for the design and suitable for steam and dry reforming of methane reactions.

1. Introduction

The need for alternative and clean energy has a significant area of interest of worldwide researchers to develop sustainable energy. Within the current significant researches, production and purification of hydrogen from syngas as well as their use in the fuel cell technology. Syngas has enormous potential in producing clean energy meets the high demands for liquid and gaseous fuels and electricity. Syngas is a promising technology to improve the energy efficiency, utilization for fuel production and electricity generation, and pollutant elimination to reduce greenhouses gas emission.

Syngas also referred as synthesis gas is the mixture of gases such as carbon monoxide, hydrogen and other gases in small quantity. This gas is produced from natural gas and other hydrocarbons. The production of syngas is performed through a reforming process by an endothermic or exothermic reaction based on the selected chemical process to implement the methane catalytic reforming. Syngas can be also produced from biomass gasification which is not the scope of the current review work.

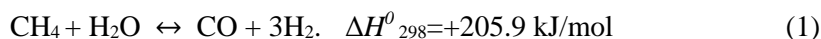


Syngas production is essential for many applications, such as producing hydrogen to be used in the processing of fuel cell from natural gas. Beside gas engine, turbines (combined cycle), Fischer-Tropsch to produce a light synthetic crude oil or heavy waxy hydrocarbons, methanol and ammonia production, etc. [1][2]. Besides, recently syngas has started to be utilized in the transport sector to enhance the performance of the internal combustion engine [3].

Syngas can be produced from different feedstock such as biomass, coal, coke and natural gas. The primary feedstock and chemical reaction path determine the H₂:CO ratio which is called syngas ratio. The reforming of natural gas is considered as the most popular method used to produce syngas by converting methane, natural gas constituent to hydrogen and carbon monoxide mixture (CO+H₂). There are several techniques of methane reforming such as steam reforming, dry reforming of carbon dioxide (CO₂), partial oxidation and Tri-reforming of natural gas using the flue gas [4]. Each process generates a syngas mixture which have different compositions of H₂:CO ratio. The reforming reaction differs in each process because it depends on several variables such as temperature and pressure of reaction. Besides, the kind of catalyst used in the reaction and these variables are essential to control the route and output of the reaction [5]. The current work is aimed at evaluating the technological progress and limitations of the different reforming processes mainly for the production of syngas thereby to layout potential recommendations for future directions. Most of the previous review works are limited to specific reforming technologies and their recommendations are limited in nature. In this regard, this review paper consists of five sections. Section 2 and Section 3 discuss the steam and dry reforming processes and their technological progress with respect to the thermodynamic analysis, reformer design, operating parameters and the advancements on the catalyst options with respect to the syngas yield. Section 4 provides the application areas in today's technological status and their future prospect. Finally, the concluding remark is provided in Section 5.

2. Steam Reforming

Steam reforming of natural gas is the process where the steam reacts endothermically and catalytically with hydrocarbon. The reaction is done inside a reformer at a temperature of 700-900°C to produce H₂ and CO mixture (syngas).



The reaction under this condition, the catalytic process of steam methane reforming (SRM) can generate syngas with high H₂:CO ratio (H₂/CO ≥ 5). Therefore, SRM is a widely used in industrial production of H₂ [6]. The steam reforming is affected by different parameters such as reaction temperature and pressure, supported catalyst and flow rate of the reactants [7,8]. Catalytic reaction (process) is vital in the reforming of natural gas for the production of synthesis gas. Among the design requirements of a steam methane reformers, bigger area for heat transfer, enough volume to contain the catalyst, enough source of heat, heat recovering mechanism, reactants feed, products collection and mechanisms for the proper distribution of the reactants are the sole which special emphasis. Currently the common reformer designs in the conversion of hydrocarbons through steam reforming are adiabatic pre-reformer, tubular fired reformers and heat exchanger reformers. Adiabatic pre-reformer is an auxiliary companion of a steam reformer if there is an excess availability of steam in the process. Such installation will increase the production capacity of synthesis gas by 10-20% with no additional consumption of energy. Another advantage of adiabatic pre-reformer is to increase lifetime of the steam reformer.

The conversion of methane to syngas through the SRM process is performed in two main steps, (a) pretreatment feeding and (b) steam reforming and the heat exchange to reach the demanded temperature of the conversion. The only required pretreatment of natural gas is the desulfurization to convert sulfur into H₂S. Then, natural gas is fed to the reformer where the reaction with steam occurs to produce H₂ and CO.

The reformer includes tubes that contain a reforming catalyst kept in a heat exchange reformer that supplies the required heat for the endothermic reaction as shown in figure 1 [9,10]. The heat exchange process is conducted in different configurations namely straight-through tubes, bayonet tube and mixing of product gas and heating gas before the heat exchange. Types (a) and (b) are normally used with all kinds of heating gas. Meanwhile, type (c) is only used when the demanded product gas is generated through the mixing heating and product gas in the presence of catalyst in the reformer.

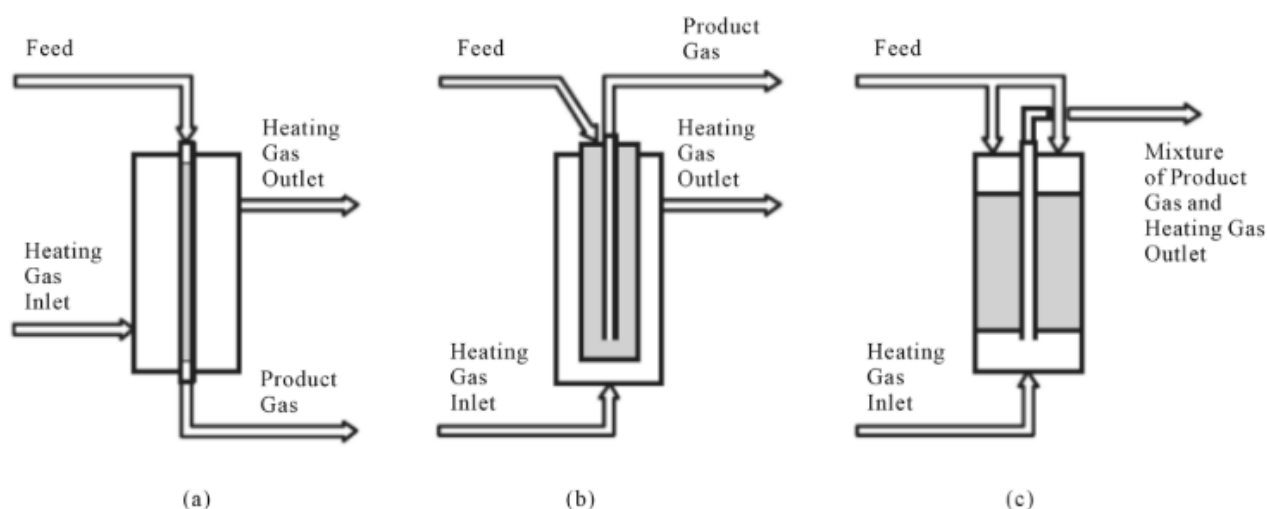


Figure 1. Different kind of heat exchange reformer, (a) straight-through tubes, (b) bayonet tube (c) mixing of product gas and heating gas before the heat exchange [9,10]

2.1 Thermodynamic analysis

As shown in the chemical Equation 1, the reaction of the SRM process is heavily endothermic ($\Delta H^{\circ}_{298} = +205.9$ kJ/mol). Therefore, the reaction is thermodynamically preferable under high temperature and low pressure. The enthalpy change (ΔH) and Gibbs free energy (ΔG°) can be calculated based on the same equilibrium constants (shown in figure 2). The SRM reaction needs a particular temperature to obtain sufficient reaction activity [11]. Figure 2 shows the change of (ΔG° and ΔH) versus the temperature during the SRM process. ΔH increases as the temperature increases whereas the ΔG° reduce. However, the low reaction temperature leads coke deposition with the time as shown in the diagram. Therefore, the SRM process needs a high temperature above 700°C [12].

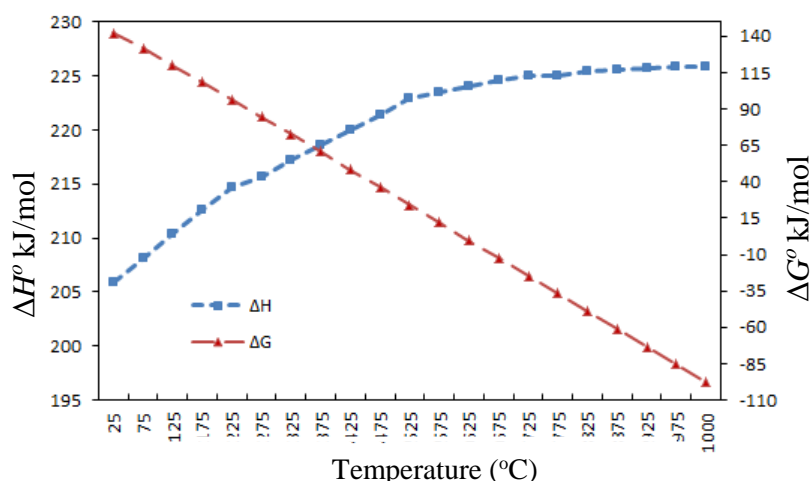


Figure 2. Variation of ΔH° and ΔG° with the reaction temperature modified from [13].

The conversion of methane depends on steam to methane ratio (S/C), and it increases with higher S/C ratio which varies from 1 to 5 steam to methane ratio. It is also influenced by the pressure and at higher pressure the conversion percentage declines. Several studies have shown that the complete conversion could be obtained at temperature of 700°C and low pressure (1.01325 bar) with (S/C > 2.5). In order to achieve a complete conversion, the reaction temperature must be above 900°C and the pressure should be above 15 bar as shown in figures 3, 4, and 5 [14]. Figure 3 shows the effect of the reforming temperature on the conversion of CH₄ and H₂O and the yield of H₂ and CO. Whereas the effect of pressure on the conversion of CH₄ and H₂O and the yield of H₂ and CO is presented in Figure 4. Similarly, the effect of mole fraction is presented in Figure 5.

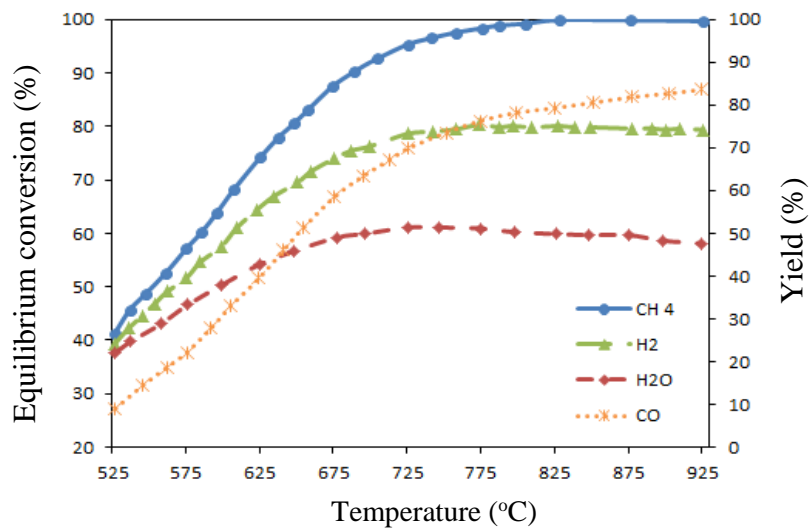


Figure 3. Effect of reforming temperature on the CH₄ and H₂O Conversion and H₂ and CO yield modified from [13,15,16].

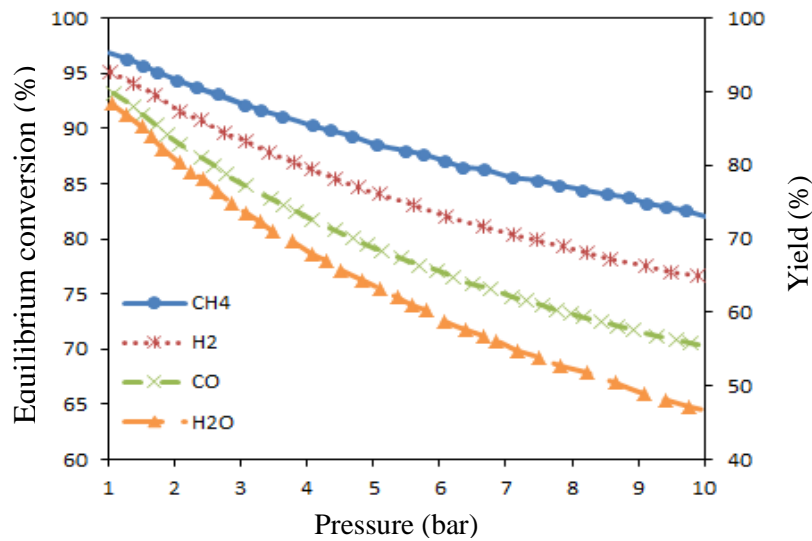


Figure 4. Effect of reforming pressure on the CH₄ and H₂O Conversion and H₂ and CO yield modified from [13,15,16].

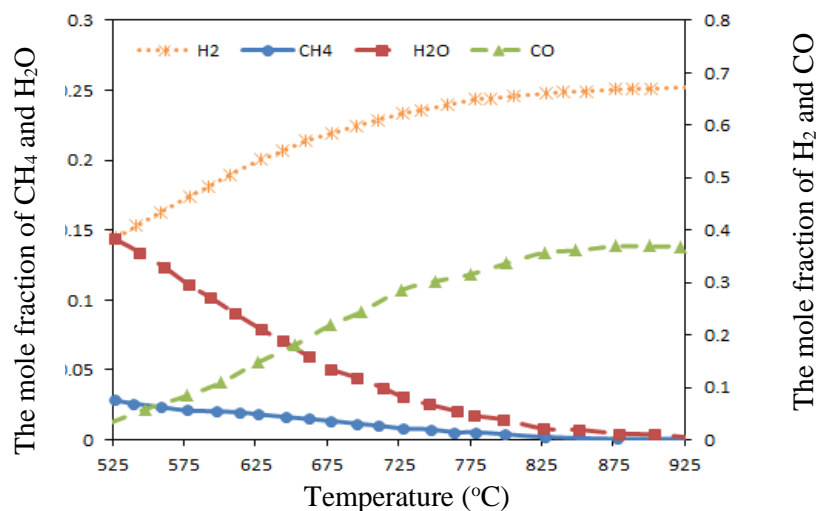
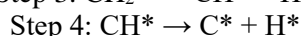
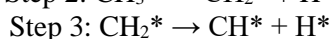
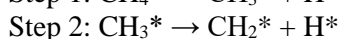
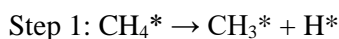


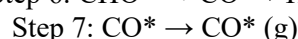
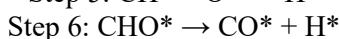
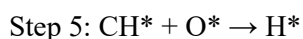
Figure 5. Effect of temperature on the mole fraction at different S/C ratio modified from [13,15,16].

2.2 Catalyst

In the majority of industrial applications, steam methane reforming (SRM) is performed at a high temperature over a Ni-based catalyst. Ni is considered to be the most preferred metal due to its sufficient activity and cost. The main problem of the Ni-based catalyst is the coke formation and Ni active metallic sintering which lead to catalyst deactivation. Due to the deactivation of the Ni-based catalyst, the new studies and current researches concentrate on a new approach involving catalyst preparation and metals reinforcement. The Ni-based has been supported by different alloys such as Ni-Co, Ni-Pt, Ni-Au [17,18]. Several studies showed that the coke suppression could be controlled in Step 4 of the reaction process during the reforming of methane as shown in the following reactions [19]:



Steps 1-4 show the mechanism of coke formation due to the reaction from adsorbed carbon cluster which causes the carbon deposition as a result of decomposition of methane. Therefore, Blaylock et al. (2009) have proposed a supplementary separation reaction such as multi-faceted Ni surface in the steam reforming [20]. Among the available reaction routes in the SRM reaction, the following steps including three Steps (5-7) were suggested to be added on top of the four steps suggested as an essential path for the reaction of methane decomposition that may avoid deposition of carbon [21].



The above reaction steps (5-7) can substitute the fourth step reaction. The added reaction produces CO instead of carbon. However, the catalyst efficiency of H₂ production will be affected. Therefore, it is necessary to understand the pathway of the reaction involving step 5-7 to minimize carbon deposition and catalytic efficiency enhancement during SRM reaction [22].

Table 1. Summary of methane steam reforming over the Ni-based catalyst at a low temperature and 1 atm pressure.

Catalyst	Ni Loading	T (°C)	S/C ratio	Time on stream (h)	CH ₄ conversion (%)	Selectivity (%)	
						CO	CO ₂
Ni/SiO ₂	Ni 20%	500	2.00	0.5	21.8	9.7	90.3
Ni/SiO ₂	Ni 20%	500	2.00	2.0	14.8	9.6	90.4
Ni/Al ₂ O ₃	Ni 20%	500	2.00	0.5	0.0	-	-
Ni/Al ₂ O ₃	Ni 20%	700	2.00	0.5	15.0	9.4	90.6
Ni/Al ₂ O ₃	Ni 20%	700	2.00	4.00	17.4	8.2	91.8
Ni/ZrO ₂	Ni 5%	500	2.00	0.5	15.6	6.9	93.1
Ni/ZrO ₂	Ni 5%	500	2.00	4.00	21.3	4.7	95.3
Ni/ZrO ₂	Ni 20%	500	2.00	0.5	14.1	13.1	86.9
Ni/ZrO ₂	Ni 20%	500	2.00	4.0	25.5	7.2	92.8

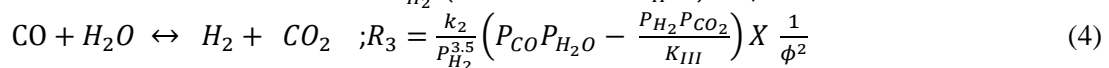
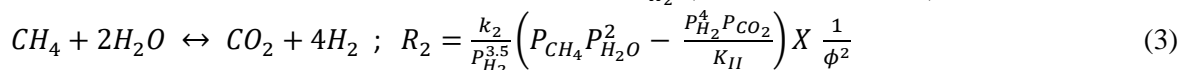
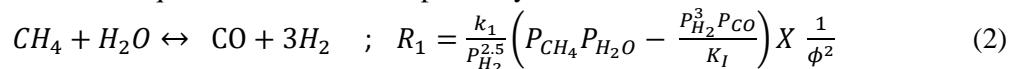
F/W: 15.0 dm³ h⁻¹ g⁻¹

The dominant kind of catalysts used in steam reforming are based on noble metals because carbon doesn't dissolve in them resulting much lower coking. Therefore, their reforming performance is high compared to other metals and the rate of carbon formation is low. However, their applications are limited due to their availability and cost [23]. Thus, leads to motivate the researchers to use Al₂O₃, SiO₂ and ZrO₂. Matsumura et al. examined Al₂O₃, SiO₂ and ZrO₂ to be used as supports and test their performance. It was found that Ni-SiO₂ started to be oxidized by the steam at 500°C. Whereas, a rapid reduction was observed in Ni-Al₂O₃ catalyst because of spinal formation of NiAl₂O₄ which results in lower activity on the surface. Furthermore, the partial oxidation of Ni-Al₂O₃ appeared after 4 hours on

the steam stream, while Ni-ZrO₂ more stability. The stability of Ni-ZrO₂ due to its assistance to form the group of hydroxyl and this is the reason beyond the higher active support of nickel in the SRM process at low temperature [24]. The effect of Ni-load and reforming temperature has indicated that the maximum catalyst is the one with 10% Ni loading at low temperature, as shown in Table 1 [15,25].

2.3 Reaction kinetics and mechanism

Diversity models of rate expressions or kinetics are proposed for SRM reaction. The parameters of kinetics are affected by the conditions of the operation and the used catalyst. In recent years, there are several studies discuss the section of the kinetics expressions involving power law, Langmuir-Hinshelwood (LH) and other expressions [16]. The kinetic expressions and reaction rate are influenced by broad range parameters such as temperature, pressure, catalysts and reactants compositions. Xu and Forment (2009) conducted several studies on LH expression. The studies have found that that, the production of CO, H₂ and CO₂ during the SRM process is the result of steam reforming and water gas shift (WGS) reactions. Besides, the formation of CO₂ is caused by the reaction of steam reforming at high S/C not only through WGS reaction. The expression of reaction rate for methane steam reforming to syngas mixture, WGS and reforming steam and methane with steam excess is provided in Equations 2, 3 and 4, respectively.



where

$$\phi = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}}$$

K = equilibrium constant.

The constants rate (k_1, k_2, k_3) for the SMR and WGS reactions and the constant of absorption (K) for the reactants and the reactions outputs were determined experimentally. The values of these constants were found based on the study by Xu and Forment (2009); and Avetnisov studies as shown in Table 2. The catalyst was used in the experiment was Ni/MgAl₂O₄ [13].

Table 2. Constants of chemical kinetic for SMR and WGS reactions

Parameters	Xu and Forment (2009) data	Avetnisov et.al data
k_1	$4.23 \times 10^{15} \exp(-240.1/RT)$	$1.97 \times 10^{16} \exp(-248.9/RT)$
k_2	$2.00 \times 10^6 \exp(-67.1/RT)$	$2.43 \times 10^5 \exp(-54.7/RT)$
k_3	$1.02 \times 10^{15} \exp(-243.9/RT)$	$3.99 \times 10^{18} \exp(-278.5/RT)$
K_{a,H_2O}	$1.77 \times 10^5 \exp(-88.68/RT)$	$9.48 \times 10^4 \exp(-74.9/RT)$
K_{a,CH_4}	$6.65 \times 10^{-4} \exp(38.28/RT)$	$6.74 \times 10^{-3} \exp(34.1/RT)$
$K_{a,CO}$	$8.23 \times 10^{-5} \exp(70.65/RT)$	$3.35 \times 10^{-4} \exp(65.5/RT)$
K_{a,H_2}	$6.12 \times 10^{-9} \exp(82.90/RT)$	$2.06 \times 10^{-9} \exp(58.5/RT)$

Wei and Iglesia [16] have conducted a study on steam reforming and CO₂ of methane over nickel-based and noble metals catalysts to watch the reforming mechanism and conversion steps. In this studies, sequences of the steps included steam and CO₂ reforming and decomposition of methane, and WGS reactions as shown in Figure 6. Methane starts to decompose to chemisorbed carbon (C*) by following H-abstraction steps. Methane decomposition becomes faster as the atoms of H are consecutively abstracted from the reactant of methane. This process caused low coverage of CH_x to C*, then chemisorbed carbon is eliminated by steam. When a sufficient amount of metal atoms is on the surface, the constant rate to activate the first C-H bond in the CH₄ will appear in the expression

rate. Therefore, the rate of the reaction becomes the first order in CH₄ and will not be influenced by the steam or co-reactant as shown in Equation 5.

$$r_f = kP_{\text{CH}_4} \quad (5)$$

where r_f is the rate of the SMR reaction, k is the constant rate, and P_{CH_4} is the partial pressure of CH₄. Additional kinetic expressions of SMR reaction of methane are shown in Table 3.

Table 3. Kinetic equations of steam methane reforming over Ni-based catalyst [13].

Catalyst	Temperature (°C)	Pressure (bar)	Rate expression	Remarks
Ni	500-900	1-15	$[hc](1 - K'5/K5)$	Design model for a plant.
Ni	500-900	1-15	$[hc](1 - K'6/K6)$	Design model for plant.
Ni	500-900	1-15	$[hc][H_2O]^2(1 - K'6/K6)$	CH ₄ produces CO ₂ then shift reversely to CO.
Industrial Ni catalyst	500-900	21-41	$\frac{[hc]}{[1 - K'5/K5][H_2]}$	A constant rate is pressure dependent due to the diffusion.
Ni foil	470-800	1-41	$\frac{[hc][H_2O]}{[H_2O]a[H_2]^2 + b[H_2]^3(1 - K'5/K5)}$	A constant rate is pressure dependent. Adsorption of hc to form CH ₂ reacts with steam (H ₂ O)
Ni/ α -AL ₂ O ₃	350-450	1-2	$\frac{[hc][H_2O]^2}{1 - a[hc][1 - K'6/K6]}$	The step of the rate determining of hc adsorption.
Ni/ AL ₂ O ₃ SiO ₂	670-770	670-770	$[hc][H_2O]^2(1 - K'6/K6)$	A constant rate is pressure dependent because of diffusion.

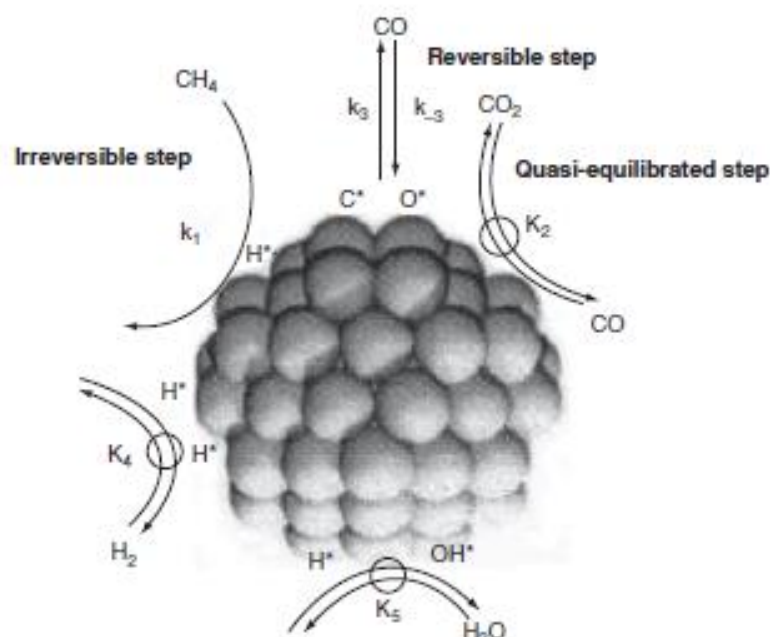
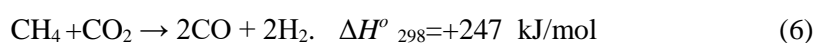


Figure 6. The sequence of elementary steps in SMR and WGS reactions [16].

3. CO₂ reforming (Dry reforming)

Dry reforming of methane (DRM) process or carbon dioxide reforming of methane is an endothermic and catalytic reaction to produce syngas. DRM is an essential process because it utilizes the most abundant greenhouse gases which are CH₄ and CO₂. The recycling of CO₂ and CH₄ is a beneficial process to produce a clean alternative fuel can be used in many applications such as hydrogen generation. Dry reforming is a reforming process like steam reforming, but it produces syngas with a lower ratio of H₂/CO. This ratio is favorable in the synthesis processes of high hydrocarbon by Fischer-Tropsch to deliver an oxygenated fuel with no needs to control the (H₂/CO) ratio by WGS reaction [26,27].

Dry reforming process (DRM) is a highly endothermic reaction demanding high energy input. DRM is a slow process including long resident time and poor transient response due to its requirements of the higher external heat exchange. However, DRM is preferred at high temperature, and low pressure and the reforming can take place in the reactor at a temperature above 640°C. But, to achieve acceptable conversion for industrial application, temperature above 800°C is needed [28,29].



3.1 Thermodynamic analysis

The thermodynamic analysis of DRM is necessary to determine the most convenience temperature, pressure and feed ratio to generate syngas with high yield. A higher temperature is needed in DRM reaction to achieve high conversion of methane and carbon dioxide to syngas. Furthermore, all kind of Ni-based catalyst reaches their highest conversion efficiency at a temperature above 800°C. Utilization of a catalyst helps to reduce the amount of demanded energy to obtain a high yield of syngas and to avoid production of derivative products higher temperature is needed [30,31].

During the DRM process, there are several reactions may occur as shown in Table 4. The table, DRM produces syngas with H₂/CO ratio ≤ 1 which is considered undesirable ratio for many industrial applications. The lower ratio refers to the simultaneous generation of CO due to the wet gas shift (WGS) reaction. There are other side reactions from WGS occurs during the reaction of CH₄ and CO₂, and most of them depend on the feed ratio (CH₄/CO₂). Besides the feed ratio, the reaction temperature and pressure affects the side reaction which includes the coke formation [32].

Table 4. Reactions in dry (CO₂) of methane [32].

Name of reaction	Equation	ΔH°_{298} (kJ/mol)
Main reaction of dry methane reforming.	$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$	+247
Reverse Side reaction.	$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$	+41
Methane decomposition.	$\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$	+74.9
CO Disproportionation (Carbon deposition.	$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$	-172.4
CO ₂ Hydrogenation.	$\text{CO}_2 + 2\text{H}_2 \leftrightarrow \text{C} + 2\text{H}_2\text{O}$	-90
CO Hydrogenation.	$\text{H}_2 + \text{CO} \leftrightarrow \text{H}_2\text{O} + \text{C}$	-131.3

From the reactions in table 4, it can be noticed that there is no direct oxygen included in the carbon gasifying which leads to carbon deposition on the surface of the catalyst. Carbon deposition is the main reason beyond the deactivation of catalyst and blockages in the reactor. Furthermore, when the reaction temperature is below 800°C, carbon formation will take place in the reaction. When the reaction temperature is higher than 800°C, the occurrence of carbon deposition during the reforming of CH₄ and CO₂ refers to the decomposition of CH₄. Therefore, reaction temperature and pressure beside the feeding rate of CH₄/CO₂ are the main parameters to control the carbon deposition and methane decomposition [33,34]. Maximum formation of carbon occurs at a temperature range of 100 to 300°C, and higher carbon formation affects the CH₄ conversion efficiency which results in the lower H₂/CO ratio [35].

Since DRM is a highly endothermic reaction, the higher conversion of CH_4 and CO_2 can be achieved. Therefore, an increase in the temperature leads to an enhancement in the rate of reaction at higher temperatures. According to thermodynamics calculation conducted by Niko and Amin, temperature above 900°C is demanded unity feed ratio of CH_4/CO_2 achieve syngas with 1:1 ratio of H_2/CO with a small amount of carbon [36]. Thus, the CH_4 conversion increases with higher temperature and an excellent yield of H_2 as shown in Figure 7. On other hands Figure 8 shows the effect of feed ratio of CH_4/CO_2 on the methane CH_4 and CO_2 conversion H_2 and CO yields at 850°C and 1 atm. It can be noticed that the lower feed ratio leads to higher CH_4 but low H_2/CO ratio which can cause higher carbon deposition and methane decomposition. At higher feed ratio 2:1 of CH_4/CO_2 , CO production became lower which produces a closer unity ratio of H_2/CO . Higher feed ratio reduces the carbon formation which causes a reduction in carbon deposition [32]. Based on Niko and Amin study, the conversion of CH_4 and CO_2 is greater at a lower pressure as shown in Figure 9 which so it is favorable to conduct the CO reforming at atmospheric pressure (1.01325 bar) [36].

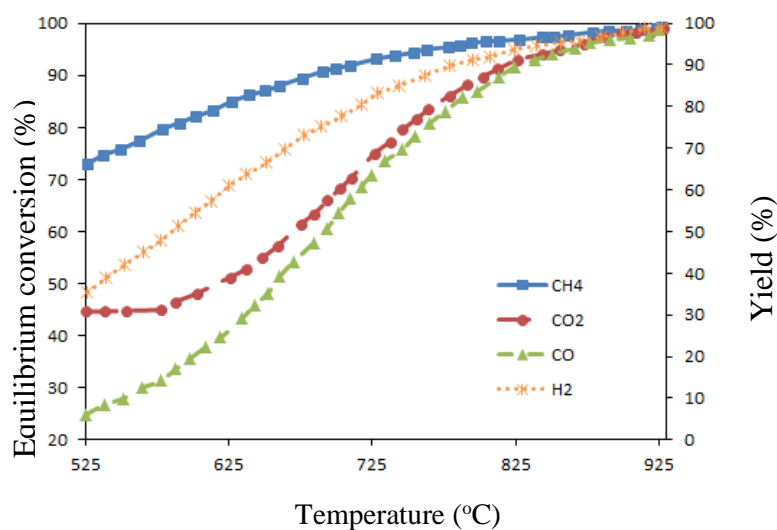


Figure 7. Effect of temperature on equilibrium conversion of CH_4 and CO_2 and yield of CO and H_2 at CH_4/CO_2 ratio of 1 modified from [32,36].

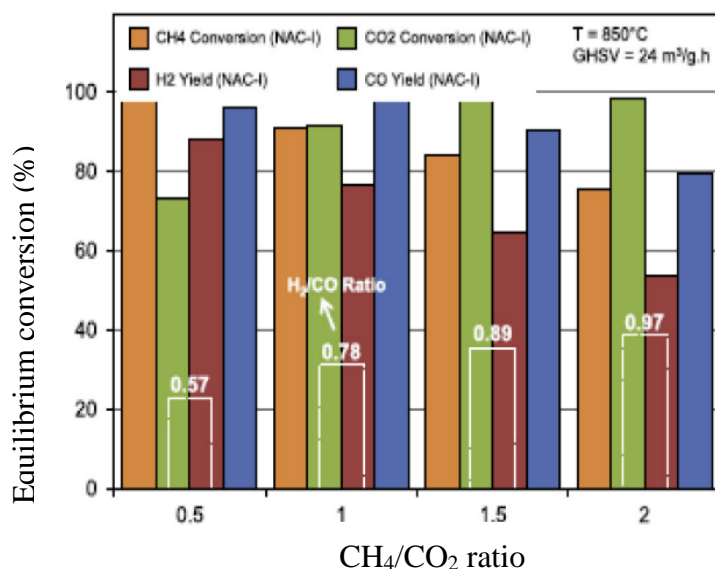


Figure 8 CH_4/CO_2 ratio on conversion of CH_4 and CO_2 and yield of CO and H_2 at 850°C and 1atm [32].

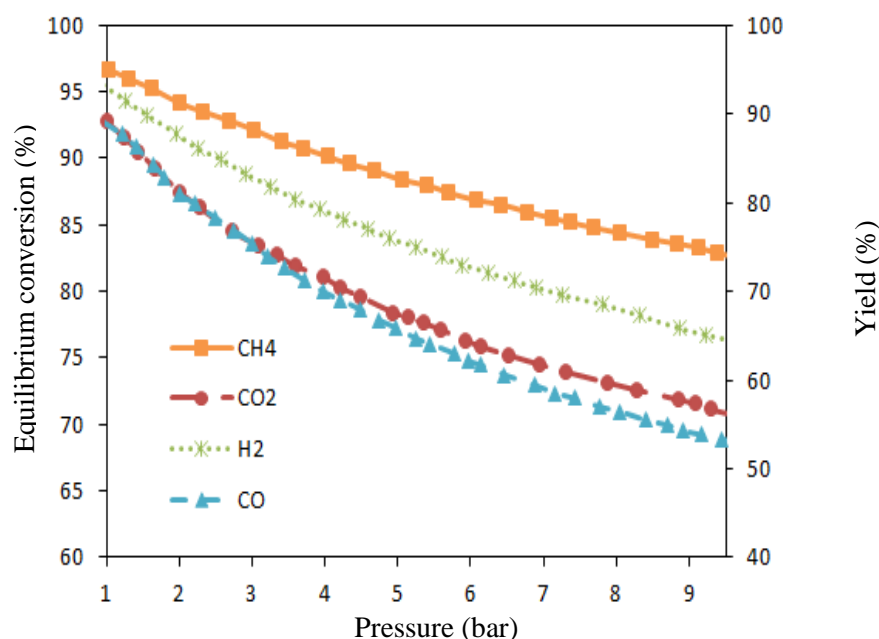


Figure 9 Effect of pressure on equilibrium conversion of CH₄ and CO₂ and yield of CO and H₂ at CH₄/CO₂ ratio of 1:1 [32,36].

3.2 Catalyst

One of the main obstacles of utilization the dry reforming process in the industrial applications is the low effectiveness of the catalysts. Thus, due to the rapid deactivation of the catalyst used in the DRM process because of the high carbon deposition. Many attempts and huge investigations have been done to develop a new catalyst can achieve high activation of CH₄ and CO₂ at low temperature. Ni-based is the most common type of catalyst used in the DRM process due to its availability and reasonable cost. They showed acceptable activity, but they deactivated rapidly due to the high carbon formation during the reaction. Nobel metals (Rh, Pd, Ru, Pt and Ir) have the highest activity for DRM process in resisting to the formation of carbon, but they are not used significantly due to their cost ineffectiveness [37].

Current studies attempt to perform a mechanistic investigation on the interaction between nickel and different supports. To modify the interaction of the Ni and their supports, carrier of composites was used to achieve higher activity at a lower temperature. Li et al. [38] have arranged a catalyst series from Ni/BaTiO₃-AL₂O₃ with various contents of BaTiO₃ for the DRM at a low temperature. It was found that the Ni/32.4 BaTiO₃-AL₂O₃ had the highest activity and it was stable for 50 h on the reactants stream. It was considered that BaTiO₃ enhanced the dispersion of the active nickel and species of NiO_x with the intensity of electron donor and then improved the catalyst stability. The equilibrium conversion of CH₄ on the following catalyst support Ni/32.4 BaTiO₃-AL₂O₃, Ni/BaTiO₃ and Ni/AL₂O₃ was 88%, 80% and 86%, respectively. The enhancement of catalyst was due to the addition of BaTiO₃ to AL₂O₃ as a result of intermittent dispersion of the particles of BaTiO₃ on the surface of AL₂O₃. The dispersion of BaTiO₃ formed individual isolated BaTiO₃ particles. Therefore, a reduction in the NiAL₂O₄ formation and that helps to strengthen the interaction between the nickel-based and the supports. The enhancement of the interaction leads to reduce the possibility of carbon deposition and improve the catalyst activity. The activity of most Ni-based catalysts for DRM at low temperature is shown in Table 5.

Table 5. Summary of the activity of Ni-based catalysts of DM at low temperature.

Catalyst	Ni loading %	Reaction conditions		Conversion %		H ₂ /CO ratio	Ref
		Temperature (°C)	Feed ratio CH ₄ /CO ₂ /N ₂	CH ₄	CO ₂		
Ni/32.4%BaTiO ₃ -AL ₂ O ₃	5	690	1:1:0	88	88	-	[38]
5% Ni/Ce _{0.6} Zr _{0.4} O ₂	5	650	1:1:0	53	43	0.92	[39]
Ni/SBA-15(RM)	10	600	1:1:0	65	88	0.83	[40]
Ni/SBA-15(PM)	10	600	1:1:0	68	75	0.87	[40]
Ni/AL ₂ O ₃ -CeO ₂	10	550	1:1:0	50	55	0.64	[41]
Ni/SiO ₂	1	500	2.2:1.8:6	7	13	0.4-0.15	[42]
Pt/Ni/Mg/Ce _{0.6} Zr _{0.4} O ₂	8	454	7:7:86	10	10	0.23	[43]
Ni/γ-AL ₂ O ₃	5	500	15:15:70	12	15	-	[44]
ZrO _x /Ni-MnO _x /SiO ₂	10	500	1:1:0	17.9	23.6	0.64	[45]
Ni/CaO/L ₂ O ₃ -ZrO ₂	5	450	1:1:1	9.8	12.9	-	[46]
NiSc/AL ₂ O ₃	11	450	1:1:0	10	12	-	[47]
Ni-Zr/SiO ₂	10	450	1:1:0	6.5	9.1	0.61	[48]
6.8%Ni/SiO ₂	6.8	450	1:1:1.8	2.9	6.5	-	[49]
1.2%Ni/TiO	1.2	450	1:1:1.8	3.2	5.9	-	[45]
Ni-Zr/SiO ₂	10	400	1:1:0	2.2	4.9	0.56	[45]
Ni/γ-AL ₂ O ₃	10	270	1:1:0	56.4	30.2	0.91	[50]
1%Ni/10%La-ZrO ₂	1	150	1:1:2	74.5	85.3	0.83	[51]

3.3 Reaction kinetics and mechanism

Kinetic investigations are used to determine the rate of the reaction model according to the theoretical mechanism of the DRM reaction. Determining the reaction rate based on the experimental data to describe the reforming process based on the theoretical chemistry which helps in catalyst selection and reactor design.

The DRM reaction mechanism is described by three models namely; the power law, Eley Redial (ER) model and Langmuir Hinshelwood-Hougen-Watson (LHW) model. Most of the studies have used the power law models due to the simplicity to apply and estimate the reaction variables. Besides, it is beneficial to solve the advanced models which demand large data [32]. The form of the kinetic rate of DRM supported by Power-Law model is shown in Equation 7.

$$r = k [PCH_4]^m [PCO_2]^n \quad (7)$$

Table 6. Mechanism of DRM reaction by Akpan et al. [52]

Reaction pathway	Elementary reaction
Adsorption	CH ₄ + 2* → CH ₃ (*)+H(*) CH ₃ (*) + * → CH ₂ (*) + H(*) CH ₂ (*) + * → CH(*) + H(*) CH(*) + * → C(*) + H(*)
Surface reaction	C(*) + O _x → CO + O _{x-1} + *
Surface reaction	CO ₂ + O _{x-1} →
Surface reaction	4 H(*) + O _x → O _{x-1} + H ₂ O
Rate of reaction	$-r_A = \frac{2.1 \times 10^{17} \exp(22800/RT) (N_A - \frac{N_C^2 N_D}{k_B N_B})}{(1 + 34.3 N_D^2)}$

Despite the advantages of the Power-law models, but they have a limitation in describing the various reactions that take place on the surface of the catalyst. Therefore, more accurate models need to be used. Akpan al et al. [52] have developed a kinetic model over Ni/CeO₂-ZrO₂ using ER model.

In this study, it was assumed that the determining step of the reaction rate is the dissociative adsorption of CH₄. The proposed model of this study investigated the reaction mechanism and the reaction rate, and it was validated with the obtained experimental data as shown in Table 6.

Table 7 Kinetic reaction models for CO₂ reforming of methane

catalyst	Reaction Pathway	Rate mode	Temperature range (°C)	Ref
Ni/ Al ₂ O ₃ , Ni/Al ₂ O ₃ - Ni/CaO	Activation of CH ₄ by Ni as RDS	$r_{ref} = \frac{aP_{CH_4} P^2_{CO_2}}{(a + P^2_{CO_2} + cP_{CH_4})}$ RDS: $*-CH_4 \rightarrow *-C + 2H_2$	500-800	[53]
Ni-Rh- Al ₂ O ₃	The surface reaction between CH ₃ and adsorbed CO ₂ as RDS	$r_{ref} = \frac{k_1 K_{CH_4} K_{CO_2} \left(\frac{P_{CH_4} P_{CO_2}}{P^{0.5}_{H_2}} - \frac{P^{1.5}_{H_2} P^2_{CO}}{K_{ref}} \right)}{\left(1 + \frac{P_{CH_4} P_{CO_2}}{P^{0.5}_{H_2} K_{CH_4}} + P_{CO_2} K_{CO_2} \right)^2}$ $k_1 = 3.59 \times 10^{21} \exp\left(\frac{332.04 \pm 52.4}{RT}\right)$ $K_{CH_4} = 2.89 \times 10^{-8} \exp\left(\frac{-109.68 \pm 57.53}{RT}\right)$ $K_{CO_2} = 3.53 \times 10^{-8} \exp\left(\frac{-125.39 \pm 39.11}{RT}\right)$ RDS: $*-CH_3 + *-CO_2 \rightarrow 2CO + 2H_2 + 2*$	505-625	[29]
Ni/SiO ₂ , MoS ₂ & WS ₂	Surface reaction between CH _X and adsorbed O as RDS	$r_{ref} = \frac{k_{ref} \sqrt{K_{CH_4} K_{CO_2} P_{CH_4} P_{CO_2}}}{\left(1 + \sqrt{K_{CH_4} P_{CH_4}} + \sqrt{K_{CO_2} P_{CO_2}} \right)^2}$ RDS: $CH_X - * + O - * \rightarrow CO + x/2H_2 + 2*$	600-800	[49]
Ni/SiO ₂	C oxidation as RDS	$r_{ref} = \frac{k_3 K_1 K_2 P_{CH_4} P_{CO_2} P_{CO} P^2_{H_2}}{\left(P_{CO} P^2_{H_2} + K_1 P_{CH_4} P_{CO} + K_2 P_{CO_2} P^2_{H_2} \right)^2}$ $K_1 = 108$ $K_2 = 22.66$ $K_3 = 4.85 \times 10^{-4} \text{ (mol s}^{-1} \text{ cat}^{-1}\text{)}$ RDS: $C-*+O-* \rightarrow CO+2*$	680-720	[29]
Ni-based	2 Step Single site RDS Activation of CH ₄ by Ni metal and decomposition of CH _X O as RDS	$r_{ref} = \frac{k_1 P_{CH_4} P_{CO_2}}{\left(\frac{k_{-1} K}{k_7} \right) P_{CO} P^{\frac{4-x}{2}}_{H_2} + \left[1 + \left(\frac{k_1}{k_7} \right) P_{CH_4} \right] P_{CO_2}}$ $k_i = k_i L, L = \text{total number of active sites}$ $K = \frac{k_8}{k_2 k_4 k_6}$ Ni/TiO ₂ : $k_1 = 0.003 - 0.042, k_7 = 0.77 - 5.53,$ $k_{-1} K = 0 - 5.38$ Ni/MgO: $k_1 = 0.0031 - 0.085, k_7 = 20.45 -$ 33.58 $k_{-1} K = 0.153 - 0.167$	400-450 ,500-550	[54]
Ni/La ₂ O ₃	2 step-single site RDS: CH ₄ activation and C gasification by adsorbed CO ₂ on metal Ni as RDS Ni/La ₂ O ₃	$r_{CH_4} = \frac{k_1 k_2 k_3 k_4 P_{CH_4} P_{CO_2}}{k_1 k_2 k_3 P_{CH_4} + k_1 k_2 P_{CH_4} + k_3 k_4 P_{CO}}$ $k_1 k_2 = 2.61 \times 10^{-3} \exp\left(\frac{-4300}{T}\right)$ $k_3 = 5.17 \times 10^{-5} \exp\left(\frac{-8700}{T}\right)$ $k_4 = 5.35 \times 10^{-1} \exp\left(\frac{-7500}{T}\right)$ RDS: $*-CH_4 \rightarrow *-C + 2H_2$ RDS ₂ : $La_2O_2CO_3 + *-C \rightarrow 4La_2O_3 + 2CO + *$	360-440	[55]

Based on the previous studies as shown in Table 7, the mechanism of DRM reaction over Ni-based catalysts include (1) CH₄ adsorption on the nickel sites in the form of dissociative for hydrogen

production beside the species of hydro-carbonate CH_x ($0 \leq x < 4$). (2) CO_2 adsorption on the support surface for the formation of carbonate and bicarbonate species, then CO_2 dissociates to CO and O which join H to form OH groups. (3) The surface of OH groups reacts with the adsorbed CH_xO to form CH_xO which is the last step for decomposition to CO and H_2 . (4) The species of CH_xO can be produced by the reaction of CH_x and O which create from the dissociation of CO_2 or split of OH group and, this step is considered as the rate determining step [29].

3.4 Other technologies of CO_2 reforming of methane

3.4.1 Dual reforming of methane of methane using Steam- CO_2

Dual reforming steam- CO_2 of methane is one of the alternative technologies to produce syngas. In dual reforming, H_2/CO ratio can be adjusted and optimized to obtain close ratio to the demanded ratio. To adjust the ratio of H_2/CO , the feed ratio $\text{CH}_4/\text{H}_2\text{O}/\text{CO}_2$ needs to be controlled. The existing of the steam in the reaction helps to reduce the coke deposition on the catalyst surfaces[56].

Li et al.[56] has conducted a study on the stability of the catalyst in the dual steam- CO_2 reforming of methane. The primary objective of the investigation was to compare the developed LA-Ni/ ZrO_2 with the classical Ni/ ZrO_2 . Figure 10 shows that higher conversion of CH_4 was obtained when the streams flow over LA-Ni/ ZrO_2 with the time on the stream. Besides LA-Ni/ ZrO_2 , showed better stability than Ni/ ZrO_2 whereas the selectivity of CO and H_2 was similar and there was no significant change was identified. The advanced performance of LA-Ni/ ZrO_2 is due to the massive interaction of Ni-support, the higher disparity of Ni, enhanced reducibility of NiO and expanded oxygen vacancies.

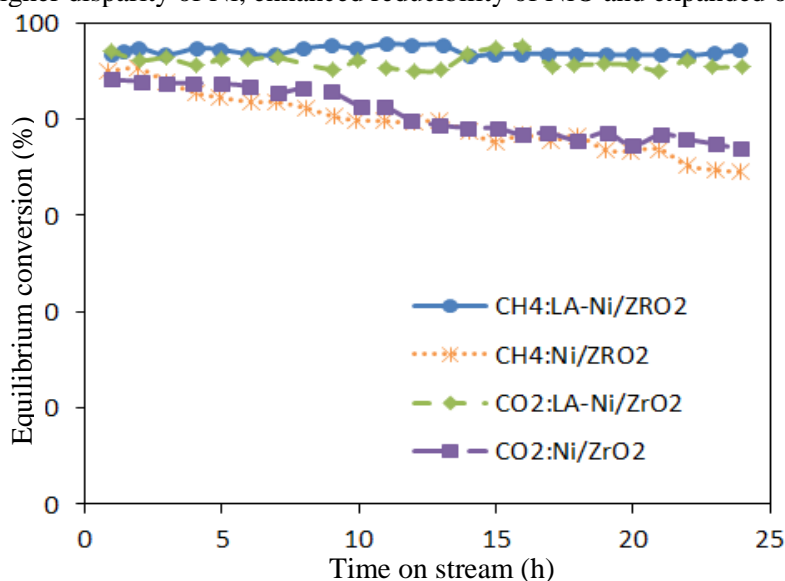
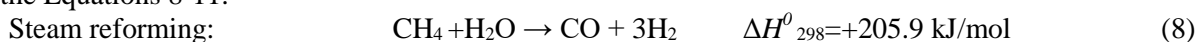
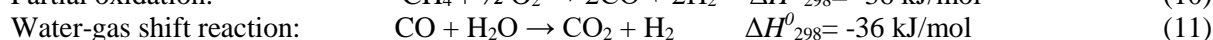
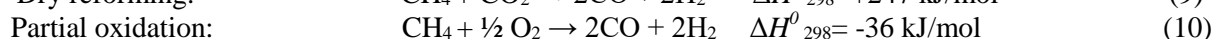


Figure 10. Conversion of CH_4 and CO_2 with the time on stream for steam- CO_2 dual reforming of methane over LA-Ni/ ZrO_2 and Ni/ ZrO_2 [56].

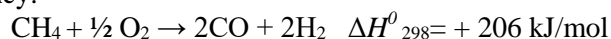
3.4.2 Tri-reforming of methane (TRM)

Tri-reforming of methane is the modern technology of syngas production with variable H_2/CO ratio. Tri-reforming of methane is a combination processes of three reforming techniques includes partial oxidation of methane, dry reforming of methane of CO_2 and steam reforming. TRM became a preferable technology because it can produce syngas with the desired ratio of H_2/CO by CO_2 which is considered as one the most abundant greenhouses gases. In TRM, H_2/CO ratio can be controlled by adjusting the feed gas to obtain exact H_2/CO . This gives an advantage of TRM to be utilized in industrial applications because it can generate syngas with the desired ratio (H_2/CO) without separating CO_2 from the exhaust gas emission like power plants flue gases [57,58]. In the TRM process, there are three reactions run simultaneously in one reactor to generate the syngas as shown in the Equations 8-11.

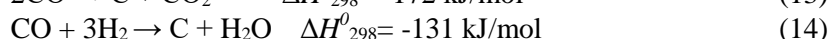
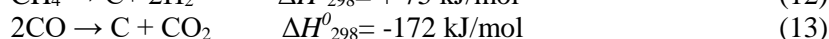
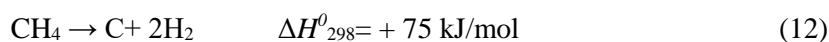




In some cases, the highly complete endothermic oxidation takes place in the reaction which leads to an increase in energy efficiency:



TRM process has more energy efficiency than SRM and DRM due to the addition of H_2O , CO_2 and O_2 at a sufficient reaction temperature range 700-900°C. Besides, it can be used in the low-quality transformation of CO_2 -rich natural gas into syngas [59, 60]. Coke formation can take place in the TRM reactions during the process of methane reforming. Coke formation usually occurs during the dispersion of methane, boudouard reaction and reduction of CO to carbon as shown in Equations 12, 13, 14 respectively [32].



Coke formation problem can be reduced by using a convenient catalyst to convert CO_2 in the presence of H_2O and O_2 . The Ni-based catalyst is the most commonly used in the TRM process due to its acceptable activity during the reaction. However, it becomes deactivated due to the coke formation. Therefore, the enhancement of the catalyst is required to improve the performance of the process by using appropriate support.

Table 8 Catalytic Tri-reforming results for different Ni–ZrO₂ catalysts by Singha et al. [61]

Catalyst	Temp (°C)	CH ₄ conv (%)	CO ₂ conv (%)	H ₂ O conv (%)	H ₂ /CO ratio
NiO	600	0	0	0	Na
	800	31	0	0	NA
5Ni–ZrO ₂ ^{ImpCom}	600	0	0	0	NA
	800	45.2	36.3	21.9	1.53
5Ni–ZrO ₂ ^{ImpCom}	600	0	0	0	NA
	800	84.4	89.3	39.9	1.62
2.3Ni–ZrO ₂ ^{HT}	600	25.3	18.5	20.9	2.12
	800	98.3	93.1	94.5	1.99
4.8Ni–ZrO ₂ ^{HT}	600	38.2	31.4	33.5	2.08
	800	98.5	98.1	98.6	1.99
9.5Ni–ZrO ₂ ^{HT}	600	32.7	23.7	24.9	2.01
	800	98.4	97.7	97.6	1.98
4.8Ni–ZrO ₂ ^{HT} (O ₂ Preheated)	600	0	0	0	NA
	800	97.6	93.2	94.8	2.21
4.8Ni–ZrO ₂ ^{HT} (H ₂ Preheated)	600	38.6	31.3	33.8	2.09
	800	98.3	98.5	98.1	1.99

Singha et al.[61] had conducted a study on the effect of Ni–ZrO₂ on the tri-reforming of methane and the coke formation during the TRM reactions. In this study, a developed catalyst Ni–ZrO₂ prepared by hydrothermal was used with different Ni loadings and preparation methods and compared with the impregnated catalyst. Ni–ZrO₂ developed by hydrothermal showed higher than another method. Impregnated catalysts were deactivated rapidly and showed unacceptable conversion rate at 600°C unlike 800°C as shown in Table 8.

In tri-reforming of methane, the feed ratio concentration has a significant effect on the equilibrium conversion of the reactants and H₂/CO ratio. In Singha et al. [61] found that when the concentration of O₂ increases in the feed ratio, CO₂ is inhibited from reforming and lower CO₂ conversion. Thus, because based on thermodynamic concepts when the amount of O₂ is high, the reaction between the oxygen and methane is more preferable than the reaction of methane with CO₂. Also, the higher oxygen concentration in the reaction motivates the maximum amount of methane to react with the oxygen which leads to reducing the available methane. However, the possibility of steam and dry reforming becomes very low.

The reactants conversion in the TRM process is influenced significantly by the steam concentration in the feed ratio. It was noticed that the existing of steam in the reaction feed causes an enhancement in steam reforming and WGS reactions. High concentration of H₂O in the reaction reduces the conversion of CO₂ because thermodynamically methane steam reforming is more preferable than dry reforming.

Table 9 Comparison between steam and dry reforming of methane reactions

Reaction type	SRM	DRM
Advantages	<ol style="list-style-type: none"> 1. High efficiency 2. Preferable for large-scale operations. 3. Favorable for large hydrogen production 	<ol style="list-style-type: none"> 1. Reforms the most tow abundant greenhouse gasses emission which is CO₂ and CH₄. 2. Clean and it doesn't have high CO₂ emission compared to the SRM process. 3. Obtain the desired H₂/CO ratio. 4. No need to separate CO₂ from the flue gases. 5. Small reformer
Disadvantages	<ol style="list-style-type: none"> 1. Needs high energy 2. Requires high cost 3. Demands high CO₂/CH₄ for greater syngas production 4. Complex system. 5. Requires large reformer 	<ol style="list-style-type: none"> 1. Rabid coke formation and deposition compared to SRM.
H ₂ /CO ratio	3:1	1:1
Operating conditions:		
Temperature	700 -1000°C	500-850°C
Pressure	3-25 bar	Atmospheric pressure
Feed ratio	CH ₄ /H ₂ O = 1:1	CH ₄ / CO ₂ = 1:1

4. Application of SRM and CO₂ Reforming

Steam reforming technology is employed for large-scale for hydrogen production from natural gas. SRM provides an efficient economical and various process for hydrogen production. Therefore, it has the highest efficiency among all the commercially available methods of hydrogen production and its production efficiency is about 65%-75% [13]. Dry reforming is considered as a promising industrial future technology for syngas production due to its simplicity compared to SRM process. Also, it is more cost-effective than SRM because it doesn't require a complex reforming system. Utilization of CO₂ without separation from its source is a beneficial method for energy saving and reduction of greenhouses gas emission. Therefore, the typical flue gas from the process of fossil fuel combustion of the power plant is capable of being used CO₂. Standard flue gases from fossil fuel and natural gas combustion are a mixture of CO₂, H₂O, O₂ and N₂ beside little impurities of SO_x, NO_x etc. Nowadays, tri-reforming of methane can be performed by using CO₂, H₂O, O₂ as a feed with the natural gas. Flue gases of power plants boiler have an excellent source with desired concentration feed for the tri-reforming process. DRM process is also considered as a very good source for hydrogen production from biogas and fuel-cell [61-63].

5. Conclusion

Form the above review; it can be concluded that SRM and DRM including dual steam-CO₂ and tri-reforming has their particularities and features. Steam reforming has the highest efficiency among all the reforming methods, but it has several challenges. Steam reforming is preferred at low pressure, high temperature and moderate feed ratio of CH₄/H₂O. Catalytic deactivation is one of the problems of SRM method at greater syngas production due to the WGS and reforming steam and methane with

steam excess. These reactions lead to increase the amount of carbon on the surface of the catalyst which leads to coke formation. LH and ER models considered the most suitable kinetic modes for SRM reactions. DRM process has a promising future because it utilizes CH₄ and CO₂ which are the most abundant in greenhouses gas emission. DRM process is thermodynamically preferred at a very high temperature above 650°C. The main problem of the DRM process is the rapid coke formation along the catalyst surface which is the main reason beyond the catalyst deactivation. Rapid deactivation problem can be avoided by adding metal supports to the Ni-based catalyst to improve the catalyst interaction which will help to enhance the catalyst performance. The standard kinetic models used in DRM reactions are power law model, LH model and ER model. The method of parameter preparation plays a major role in the performance of the catalyst and reforming efficiency as well.

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